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(54) Process for the preparation of hydrocarbons.

(57) Syngas with a H₂/CO mol.ratio between 0.75 and 1.75 is converted into hydrocarbons by contacting it first with a special cobalt-containing Fischer-Tropsch catalyst under such conditions that the conversion lies within a specified range depending on the H₂/CO mol.ratio of the syngas feed, and thereafter, after water removal, with a catalyst composition comprising both hydrocarbon synthesis- and CO-shift activity. A high H₂ + CO-conversion combined with a high C₅⁺ selectivity can be obtained starting from a syngas with a H₂/CO mol.ratio (F) between 0.75 and 1.75 by carrying out the process in two stages as described hereinbefore under such conditions that in the first stage the following relation is met:

$$150 \times \frac{f-0.5}{f+1} < C < 250 \times \frac{F-0.5}{F+1}$$

In which C represents the H₂ + CO-conversion in mol.%,

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K 5733

PROCESS FOR THE PREPARATION OF HYDROCARBONS

The invention relates to a process for the preparation of hydrocarbons by catalytic conversion of a mixture of carbon monoxide and hydrogen.

The preparation of hydrocarbons from a H_2/CO mixture by
5 contacting this mixture at elevated temperature and pressure with a catalyst is known in the literature as the Fischer-Tropsch hydrocarbon synthesis. Catalysts often used for the purpose comprise one or more metals from the iron group, together with one or more promoters, and a carrier material. These catalysts can suitably
10 be prepared by the known techniques, such as precipitation, impregnation, kneading and melting. The products which can be prepared by using these catalysts generally have a very wide molecular weight distribution range and, in addition to branched and unbranched paraffins, they often contain considerable amounts of
15 olefins and oxygen-containing organic compounds. Usually only a minor portion of the products obtained is made up of middle distillates. Of these middle distillates not only the yield but also the pour point is unsatisfactory. Therefore the direct conversion of H_2/CO mixtures according to Fischer-Tropsch is not a very
20 attractive route for the production of middle distillates on a technical scale.

In this patent application "middle distillates" should be taken to be hydrocarbon mixtures whose boiling range corresponds substantially with that of the kerosine and gas oil fractions
25 obtained in the conventional atmospheric distillation of crude mineral oil. The middle distillate range lies substantially between about 150 and 360°C.

Recently there was found a class of Fischer-Tropsch catalysts having the property of yielding a product in which only very minor
30 amounts of olefins and oxygen-containing compounds occur and which

consists virtually completely of unbranched paraffins, a considerable portion of which paraffins boils above the middle distillate range. It has been found that by hydrocracking the high-boiling part of this product can be converted in high yield into middle
5 distillates. As feed for the hydrocracking at least the part of the product is chosen whose initial boiling point lies above the final boiling point of the heaviest middle distillate desired as end product. The hydrocracking, which is characterized by a very low hydrogen consumption, leads to middle distillates which have
10 a considerably better pour point than those obtained in the direct conversion of a H_2/CO mixture according to Fischer-Tropsch.

The Fischer-Tropsch catalysts belonging to the afore-mentioned class contain silica, alumina or silica-alumina as carrier material and cobalt together with zirconium, titanium and/or chromium as catalytically active metals, in such quantities that per
15 100 pbw of carrier material the catalysts comprise 3-60 pbw of cobalt and 0.1-100 pbw of zirconium, titanium or chromium. The catalysts are prepared by depositing the metals involved on the carrier material by kneading and/or impregnation. For further information on the preparation of these catalysts by kneading and/or
20 impregnation reference may be made to Netherlands Patent Application No. 8301922 recently filed in the name of the Applicant.

When the present cobalt catalysts are used for the Fischer-Tropsch hydrocarbon synthesis starting from H_2/CO -mixtures having
25 a H_2/CO molar ratio of about 2, very high H_2+CO conversions can be achieved. However, when feeds with a lower H_2/CO molar ratio are used, the H_2+CO conversion is insufficient. The H_2+CO conversion is seen to be lower according as the feed has a lower H_2/CO molar ratio.

30 Since nature provides large amounts of material with a relatively low H/C ratio, such as coal, which when converted into H_2/CO mixtures yields products having a H_2/CO molar ratio lower than 2, it would naturally be very welcome if a way could be found to solve the afore-mentioned problem of low H_2+CO conversions.

During an investigation into this subject two measures were found which have made it possible to realise high H₂+CO conversions in the hydrocarbon synthesis starting from H₂/CO mixtures having H₂/CO molar ratios between 0.25 and 1.75 and by using the present cobalt catalysts. In addition the application of these measures leads to a high C₅⁺ selectivity. By the first measure the H₂/CO mixture is converted over a mixture of two catalysts, one of which is the cobalt catalyst and the other a copper- and zinc-containing composition. By the second measure the H₂/CO mixture is first partly converted over the cobalt catalyst, and subsequently the unconverted H₂ and CO is converted over a bi-functional catalyst or catalyst combination which, in addition to activity for the conversion of a H₂/CO mixture into hydrocarbons, has activity for the conversion of a mixture of H₂O and CO into a mixture of H₂ and CO₂.

Conditional upon the H₂/CO molar ratio of the feed to be converted it is either exclusively measure 1, or exclusively measure 2, or either one of the two measures that is eligible for use. For feeds with a H₂/CO molar ratio between 0.25 and 0.75 only measure 1 is applicable. If the feed has a H₂/CO molar ratio between 1.0 and 1.75, it is only measure 2 that is eligible. For feeds with a H₂/CO molar ratio between 0.75 and 1.0 either measure 1 or measure 2 can be used at choice.

The present patent application relates to the use of measure 2 for feeds with a H₂/CO molar ratio between 0.75 and 1.75. The use of measure 1 for feeds having a H₂/CO molar ratio between 0.25 and 1.0 forms the subject matter of Netherlands Patent Application (K 5723).

The partial conversion which in accordance with measure 2 is carried out in the first step of the process should be performed under such conditions as to satisfy the relation

$$150 \times \frac{F-0.5}{F+1} < C < 250 \times \frac{F-0.5}{F+1},$$

wherein F represents the H₂/CO molar ratio of the feed and C the H₂+CO conversion, expressed as %mol. After the water formed has

been removed from the product of the first step at least the unconverted H_2 and CO thereof should be contacted in the second step with the bifunctional catalyst or catalyst combination mentioned hereinbefore.

5 The present patent application therefore relates to a process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, in which a H_2 - and CO-containing feed having a H_2 /CO molar ratio (F) in the range between 0.75 and 1.75 is contacted in the first step with a catalyst comprising 3-60 pbw
10 of cobalt and 0.1-100 pbw of at least one other metal chosen from the group formed by zirconium, titanium and chromium per 100 pbw of silica, alumina or silica-alumina, which catalyst has been prepared by kneading and/or impregnation, the contact being brought about under such conditions as to satisfy the relation

15
$$150 \times \frac{F-0.5}{F+1} < C < 250 \times \frac{F-0.5}{F+1},$$

wherein C represents the H_2 +CO conversion expressed as %mol, and in which of the product from the first step - after removal of the water formed - at least the H_2 and CO that has remained unconverted is contacted in a second step with a catalyst or catalyst
20 combination which, in addition to activity for the conversion of a mixture of H_2 and CO into hydrocarbons, has activity for the conversion of a mixture of H_2O and CO into a mixture of H_2 and CO_2 .

25 In the process of the invention it is preferred to use in the first step the cobalt catalysts which form the subject matter of Netherlands patent application No. 8301922. These are catalysts which satisfy the relation

$$(3 + 4 R) > \frac{L}{S} > (0.3 + 0.4 R), \text{ wherein}$$

30 L = the total quantity of cobalt present in the catalyst, expressed as mg Co/ml catalyst,
S = the surface area of the catalyst, expressed as m^2 /ml catalyst,
and

R = the weight ratio of the quantity of cobalt deposited on the catalyst by kneading to the total quantity of cobalt present in the catalyst.

5 The preparation of the cobalt catalysts used in the first step of the process of the invention is preferably carried out by one of the three procedures mentioned hereinafter:

- a) first cobalt is deposited in one or more steps by impregnation and subsequently the other metal is deposited in one or more steps, also by impregnation,
- 10 b) first the other metal is deposited in one or more steps by impregnation and subsequently the cobalt is deposited in one or more steps, also by impregnation, and
- c) first cobalt is deposited in one or more steps by kneading and subsequently the other metal is deposited in one or more steps
15 by impregnation.

In the process according to the invention preference is given to the use of cobalt catalysts containing 15-50 pbw of cobalt per 100 pbw of carrier. The preferred quantity of other metal present in the cobalt catalysts depends on the way in which this metal has
20 been deposited. In the case of catalysts where first cobalt has been deposited on the carrier, followed by the other metal, preference is given to catalysts containing 0.1-5 pbw of the other metal per 100 pbw of carrier. In the case of catalysts where first the
25 other metal has been deposited on the carrier, followed by the cobalt, preference is given to catalysts containing 5-40 pbw of the other metal per 100 pbw of carrier. Preference is given to zirconium as other metal and to silica as carrier material. Preparatory to being suitable for use the cobalt catalysts should first be activated. This activation may suitably be carried out by
30 contacting the catalyst at a temperature between 200 and 350°C with hydrogen or a hydrogen-containing gas.

In the process according to the invention from the product of the first step - after removal of the water formed - at least the H₂ and CO that has remained unconverted is contacted in a second

step with the bifunctional catalyst or catalyst combination mentioned hereinbefore. It is preferred to divide the product of the first step by cooling into a gaseous fraction substantially consisting of unconverted H_2 and CO , and C_4^- hydrocarbons, and a
5 liquid fraction substantially consisting of C_5^+ hydrocarbons and water, and to use the gaseous fraction as feed for the second step. Optionally the total reaction product of the first step may be used - after removal of water - as feed for the second step.

As examples of catalysts and catalyst combinations eligible
10 for use in the second step of the process according to the invention may be mentioned:-

- 1) Catalysts prepared by impregnation which comprise 5-50 %w of iron and 5-50 %w of copper and zinc supported on a carrier and in which the weight ratio of the total quantity of copper and
15 zinc to the quantity of iron is 0.5-5. When such catalysts are used preference is given to catalysts whose Cu/Zn atomic ratio lies between 0.25 and 4 and in which the weight ratio of the total quantity of copper and zinc to the quantity of iron lies between 1.0 and 3.0. Examples of such catalysts are
20 Fe/K/Cu/Zn/SiO₂ catalysts..
- 2) Catalysts prepared by impregnation which comprise 30-75 pbw of iron and 5-40 pbw of magnesium per 100 pbw of alumina. When such catalysts are used preference is given to catalysts comprising
25 40-60 pbw of iron and 7.5-30 pbw of magnesium per 100 pbw of alumina. Examples of such catalysts are Fe/K/Cu/Mg/Al₂O₃ catalysts.
- 3) Catalysts prepared by impregnation which comprise 10-40 pbw of iron and 0.25-10 pbw of chromium per 100 pbw of silica. When such catalysts are used preference is given to catalysts comprising
30 20-35 pbw of iron and 0.5-5 pbw of chromium per 100 pbw of silica. Examples of such catalysts are Fe/K/Cr/SiO₂.
- 4) Catalyst mixtures obtained by mixing a crystalline metal silicate of a special structure either with one of the iron catalysts mentioned under 1)-3), or with a ZnO/Cr₂O₃ catalyst,

or with a Cu/ZnO/Cr₂O₃ catalyst, or with a mixture of a Cu/ZnO/Cr₂O₃ catalyst and gamma-Al₂O₃.

The crystalline metal silicates mentioned under 4) are characterized in that after one hour's calcination in air at 500°C,
5 they have the following properties

a) an X-ray powder diffraction pattern in which the four lines mentioned in Table A are the strongest lines

Table A

d(Å)

11.1 ± 0.2

10.0 ± 0.2

3.84 ± 0.07

3.72 ± 0.06 , and

b) in the formula which represents the composition of the silicate expressed in moles of the oxides and in which, in addition to
10 SiO₂, one or more oxides of a trivalent metal M, chosen from the group formed by aluminium, iron and gallium, are present, the SiO₂/M₂O₃ molar ratio is higher than 10.

Since it is desirable to prepare in the process according to the invention so large an amount as possible of a product which
15 can be converted into middle distillates by hydrocracking, it is preferred to use in the second step a catalyst combination in which the activity for the conversion of a H₂/CO mixture into hydrocarbons originates in a cobalt catalyst belonging to the same class as that from which the cobalt catalyst used in the first step was
20 chosen. When such a cobalt catalyst is used in the second step, the same preference applies with regard to method of preparation and composition as mentioned for the cobalt catalyst used in the first step.

In the process according to the invention preference is given
25 in the second step to the use of a mixture of two catalysts, the one catalyst being a cobalt catalyst belonging to the same class as that from which the cobalt catalyst used in the first step was chosen, and the other catalyst being a copper- and zinc-containing

composition having a Cu/Zn atomic ratio between 0.1 and 10. Special preference is given to such catalyst mixtures wherein the two catalysts are present in such a ratio that the (Cu+Zn)/Co atomic ratio in the catalyst mixture lies between 0.5 and 5. The copper- and zinc-containing composition present in the catalyst mixture preferably has a Cu/Zn atomic ratio between 0.25 and 4. Preparatory to being eligible for use the catalyst mixtures containing a cobalt catalyst and a copper- and zinc-containing composition should be activated. This activation may suitably be carried out by contacting the catalyst mixture with hydrogen or a hydrogen-containing gas, first at a temperature between 150 and 250°C and subsequently at a higher temperature, between 200 and 350°C.

The process according to the invention is preferably carried out at a temperature of 125-350°C and a pressure of 5-100 bar. Special preference is given to a temperature of 175-275°C and a pressure of 10-75 bar.

As stated hereinbefore, the present cobalt catalysts when used for the conversion of a H₂- and CO-containing feed yield a substantially waxy product whose high-boiling part can be converted in high yield into middle distillates by a hydrocracking treatment. This is also true when use is made not of the cobalt catalysts alone but of the above-described catalyst mixtures containing such cobalt catalysts.

Although, when the products prepared over the present cobalt catalysts or over catalyst mixtures containing the present cobalt catalysts are used in the preparation of middle distillates, the part of those products whose initial boiling point lies above the final boiling point of the heaviest middle distillate desired as end product will do as feed for the hydrocracking, it is preferred to use for this purpose the total C₅⁺ fraction of said products, since it has been found that the catalytic hydrotreatment leads to enhanced quality of the gasoline, kerosine and gas oil fractions present therein.

The hydrocracking is carried out by contacting the fraction to be treated at elevated temperature and pressure and in the pre-

sence of hydrogen with a catalyst comprising one or more noble metals from Group VIII supported on a carrier. The hydrocracking catalyst used by preference is a catalyst comprising 0.1-2 %w, and in particular 0.2-1 %w, of one or more noble metals from Group VIII. supported on a carrier. Preference is given to catalysts containing platinum or palladium as Group VIII noble metal and silica-alumina as carrier. The hydrocracking is preferably carried out at a temperature of 200-400°C and in particular of 250-350°C and a pressure of 5-100 bar and in particular of 10-75 bar.

10 The invention is now illustrated with the aid of the following example:

Example

Catalyst 1 and Catalyst 2 were mixed together to compose Catalyst Mixture I.

15 Catalyst 1

Co/Zr/SiO₂ catalyst which comprised 25 pbw of cobalt and 0.9 pbw of zirconium per 100 pbw of silica and had been prepared by single-step impregnation of a silica carrier with a solution of cobalt nitrate in water, followed by single-step impregnation of the cobalt-loaded carrier with a solution of zirconium nitrate in water. In both impregnation steps the quantity of solution used had a volume which corresponded substantially with the pore volume of the carrier. After the two impregnation steps the material was dried and then calcined at 500°C. The catalyst had a value for L of 98 mg/ml and for S of 96 m²/ml, and consequently it had a value for L/S of 1.02 mg/m².

Catalyst 2

Cu/Zn/Al₂O₃ catalyst comprising 24.3 %w of copper and 38.0 %w of zinc and therefore having a Cu/Zn atomic ratio of 0.66.

30 Catalyst Mixture I

Catalysts 1 and 2 were mixed in such a ratio as to obtain a Catalyst Mixture I, whose (Cu+Zn)/Co atomic ratio was 3.75.

Catalyst testing

Catalyst 1 and Catalyst Mixture I were used in eight experiments

(1-8) in the preparation of hydrocarbons from mixtures of carbon monoxide and hydrogen. The experiments were carried out at a space velocity of 10 Nl feed per hour and at a pressure of 20 bar in one or two reactors containing a fixed catalyst bed of Catalyst 1 or Catalyst Mixture I. Experiments 1 and 2 were carried out in a single step by using Catalyst 1. Experiment 8 was also carried out in a single step, but using Catalyst Mixture I. Experiments 3-7 were carried out in two steps by using Catalyst 1 in the first step and Catalyst Mixture I in the second step. In the two-step experiments the reaction product from the first step was cooled to divide it into a gaseous fraction substantially consisting of unconverted H_2 and CO, and C_4^- hydrocarbons, and a liquid fraction substantially consisting of C_5^+ hydrocarbons and water, and the gaseous fraction was used as feed for the second step. Preparatory to the testing Catalyst 1 and Catalyst Mixture I were activated by contacting them with a hydrogen-containing gas; Catalyst 1 at $250^\circ C$; Catalyst Mixture I first at $200^\circ C$ and subsequently at $250^\circ C$. The results of the experiments and the H_2/CO molar ratios (F) of the feeds used in each of the experiments as well as the reaction conditions are listed in the table.

The parameters C, total H₂+CO conversion, and total C₅⁺ selectivity used in the table are defined as follows:-

$$C = \frac{\text{mol H}_2\text{+CO present in feed} - \text{mol H}_2\text{+CO present in product of first step}}{\text{mol H}_2\text{+CO present in feed}} \times 100$$

$$\text{Total H}_2\text{+CO conversion} = \frac{\text{mol H}_2\text{+CO present in feed} - \text{mol H}_2\text{+CO present in product of second step}}{\text{mol H}_2\text{+CO present in feed}} \times 100$$

$$\text{Total C}_5^+ \text{ selectivity} = \frac{\text{pbw C}_5^+ \text{ hydrocarbons present in product of first+second step}}{\text{pbw hydrocarbons present in product of first +second step}} \times 100$$

TABLE

Exp. No.	Reaction step No.	Quantity of catalyst, ml	F	Temp., °C	C, % mol	Total H ₂ +CO conversion % mol	Total C ₅ ⁺ selectivity, %w
1	-	20	1.0	220	-	68	88
2	-	20	1.0	230	-	74	87
3	1 2	6.5 13.5	1.0	230 250	48	91	86
4	1 2	6.5 13.5	1.0	245 250	66	81	86
5	1 2	3 17	1.0	220 250	18	86	75
6	1 2	6.5 13.5	1.5	235 250	76	99	84
7	1 2	3 17	1.5	225 250	30	77	72
8	-	20	1.5	250	-	63	55

K 5733

C L A I M S

1. A process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, characterized in that a H₂- and CO-containing feed having a H₂/CO molar ratio (F) in the range between 0.75 and 1.75 is contacted in the first step with a catalyst comprising 3-60 pbw of cobalt and 0.1-100 pbw of at least one other metal chosen from the group formed by zirconium, titanium and chromium per 100 pbw of silica, alumina or silica-alumina, which catalyst has been prepared by kneading and/or impregnation, the contact being brought about under such conditions as to satisfy the relation

$$150 \times \frac{F-0.5}{F+1} < C < 250 \times \frac{F-0.5}{F+1},$$

wherein C represents the H₂+CO conversion expressed as %mol, and in which of the product from the first step - after removal of the water formed - at least the H₂ and CO that has remained unconverted is contacted in a second step with a catalyst or catalyst combination which, in addition to activity for the conversion of a mixture of H₂ and CO into hydrocarbons, has activity for the conversion of a mixture of H₂O and CO into a mixture of H₂ and CO₂.

2. A process as claimed in claim 1, characterized in that in the first step a catalyst is used which satisfies the relation

$$(3 + 4 R) > \frac{L}{S} > (0.3 + 0.4 R), \text{ wherein}$$

L = the total quantity of cobalt present in the catalyst, expressed as mg Co/ml catalyst,

S = the surface area of the catalyst, expressed as m²/ml catalyst, and

R = the weight ratio of the quantity of cobalt deposited on the carrier by kneading to the total quantity of cobalt present in the catalyst.

3. A process as claimed in claim 1 or 2, characterized in that in the first step use is made of a catalyst which per 100 pbw carrier comprises 15-50 pbw of cobalt and either 0.1-5 pbw of the other metal if during the preparation cobalt was deposited first and the other metal next, or 5-40 pbw of the other metal if in the preparation the other metal was deposited first and cobalt next.
4. A process as claimed in any one of claims 1-6, characterized in that in the first step use is made of a catalyst comprising zirconium as other metal and silica as carrier.
5. A process as claimed in any one of claims 1-4, characterized in that the product from the first step is divided by cooling into a gaseous fraction substantially consisting of unconverted H_2 and CO and C_4^- hydrocarbons, and a liquid fraction substantially consisting of C_5^+ hydrocarbons and water, and that the gaseous fraction is used as feed for the second step.
6. A process as claimed in any one of claims 1-5, characterized in that in the second step use is made of a catalyst combination in which the activity for the conversion of a H_2 /CO mixture into hydrocarbons originates in a cobalt catalyst as defined in claim 1.
7. A process as claimed in claim 6, characterized in that in the second step use is made of a mixture of two catalysts, the one catalyst being a cobalt catalyst as defined in claim 1 and the other catalyst being a copper- and zinc-containing composition having a Cu/Zn atomic ratio in the range between 0.1 and 10.
8. A process as claimed in claim 7, characterized in that the two catalysts are present in the catalyst mixture in such a ratio that the (Cu+Zn)/Co atomic ratio in the catalyst mixture lies between 0.5 and 5.
9. A process as claimed in claim 7 or 8, characterized in that the copper- and zinc-containing composition has a Cu/Zn atomic ratio in the range between 0.25 and 4.
10. A process as claimed in any one of claims 1-9, characterized in that it is carried out at a temperature of 125-350°C and a pressure of 5-100 bar.